

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Magnetic Properties of Electron Beam Evaporated CoPt Alloy Thin Films

Y. YAMADA, T. SUZUKI and E. N. ABARRA, *IEEE Trans. Magn.*, 1998, **34**, (2), 343–345

Magnetic and structural studies of Co₇₅Pt₂₅ alloy thin films showed a large perpendicular magnetic anisotropy of $> 1.0 \times 10^7$ erg cm⁻³ for films deposited onto Al₂O₃(0001), Al₂O₃(11 $\bar{2}$ 0) and MgO(111) substrates at 230–450°C. The Co₃Pt h.c.p. ordered state is a plausible origin of the strong anisotropy, especially in those films with a substrate temperature of $> 300^\circ\text{C}$.

Oxidation and Corrosion Behaviour of Fe-Cr and Fe-Cr-Al Alloys with Minor Alloying Additions

I. M. WOLFF, L. E. IORIO, T. RUMPF, P. V. T. SCHEERS and J. H. POTGIETER, *Mater. Sci. Eng. A*, 1998, **241**, (1–2), 264–276

The oxidation and corrosion properties of Fe-40Cr (1) and Fe-35Cr-5Al (2) alloys modified by microalloying with Ru and rare-earth metals were studied. Microalloying with 0.2 wt.% Ru promoted the formation of a Cr-rich layer at the surface which, in (2), resulted in enhanced oxidation resistance, accompanied by strong segregation of the Ru to the outer Al oxide layer. In (1), the Ru addition was associated with an initially higher oxidation rate and an increased tendency to spalling. Small Ru additions enhance the corrosion and pitting resistance of (2).

CHEMICAL COMPOUNDS

First Example of Binuclear Complex with Pt-Re Bond Containing Bridged Nitrogen Atoms

S. E. NEFEDOV, A. A. SIDOROV, A. V. RESHETNIKOV, M. O. PONINA and I. L. EREMENKO, *Izv. RAN, Ser. Khim.*, 1998, (4), 751–752

Under UV irradiation in *m*-xylene at 80°C, the interaction of Re(CO)₅Cl and PtL₂ (L = 1,2-N(NPh)₂C₆H₄) in the presence of KOH resulted in the formation of a new heterobinuclear Pt complex, (OC)Pt[μ-N,N'-N(NPh)₂C₆H₄]₂ReCl[NH(NPh)₂C₆H₄]. This contains a Pt-Re bond of length 3.055(1) Å.

Precious Metal Polymers: Platinum or Gold Atoms in the Backbone

R. J. PUDDPHATT, *Chem. Commun.*, 1998, (10), 1055–1062

The synthesis and characterisation of oligomers and polymers containing Pt or Au atoms in the backbone are reported. The polymers vary in structure from hyperbranched or dendrimeric materials containing octahedral Pt(IV) centres to conjugated, rigid-rod type structures containing linear Au(I) centres.

ELECTROCHEMISTRY

CO Oxidation on Smooth and High Area Pt, Pt-Ru and Pt-Sn Electrodes

YU. MORIMOTO and E. B. YEAGER, *J. Electroanal. Chem.*, 1998, **441**, (1–2), 77–81

The effects and roles of Ru and Sn on CO_{ad} oxidation were studied using smooth and high area Pt, Pt-Sn and Pt-Ru electrodes. For high area Pt, Pt-Ru promoted CO_{ad} oxidation at chemical potentials where oxidation was hard, while Pt-Sn promoted oxidation at chemical potentials easily oxidised. The ternary system, Pt-Ru-Sn, had even higher catalytic activity.

Electrochemical Investigations of Bare and Pd-Coated LaNi_{4.25}Al_{0.75} Electrodes in Alkaline Solution

G. ZHENG, B. N. POPOV and R. E. WHITE, *J. Appl. Electrochem.*, 1998, **28**, (4), 381–385

Electrochemical studies on electrodes made from bare and Pd-coated LaNi_{4.25}Al_{0.75} particles are reported. The Pd coating increases the discharge capacity of the bare alloy from 125 to 290 mA h g⁻¹, which is ~74% of the theoretical value. This increase may be due to Pd hydride formation. A Pd-coated alloy electrode has lowered contact resistance.

PHOTOCONVERSION

Highly Active Visible-Light Photocatalysts for Curing a Ceramic Precursor

A. GUO, B. E. FRY and D. C. NECKERS, *Chem. Mater.*, 1998, **10**, (2), 531–536

The use of Pt(II) bis(benzoylacetate), Pt(II) bis(trifluoroacetylacetate) and Pt(II) bis(benzoyltrifluoroacetate) as visible-light-absorbing complexes for photocuring the SiC precursor oligo(methylsilylene)methylene, by hydrosilation cross-linking with tetra vinylsilane is reported. The liquid polymer is transformed to a solid within minutes, thus allowing rapid deposition of light-formed preceramic patterns.

[{Pt(CN)(C₁₀H₂₁N₄)₆}]₆: A Luminescent Hexanuclear Platinum(II) Macrocyclic Containing Chelating Dicarbene and Bridging Cyanide Ligands

S.-W. LAI, K.-K. CHEUNG, M. C.-W. CHAN and C.-M. CHE, *Angew. Chem. Int. Ed.*, 1998, **37**, (1/2), 182–184

The crystal structure of a luminescent Pt₆ macrocycle, [{Pt(CN)(C₁₀H₂₁N₄)₆}]₆, with cyclic dicarbene and bridging cyanide ligands is described. The absorption spectrum in MeOH shows an intense band at 356 nm. The high extinction coefficient indicates a spin-allowed charge-transfer transition. The long life and high energy of this excited state show that the Pt(II) species can undergo bimolecular photoreactions.

A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting

O. KHAJEV and J. A. TURNER, *Science*, 1998, **280**, (5362), 425–427

Direct H₂O electrolysis was achieved using a new, integrated, monolithic PEC/PV device of a sandwich-type patterned after the GaInP₂/GaAs *p/n*, *p/n* tandem cell but with the top *p/n* junction being replaced with a PEC Schottky-type junction. GaAs is the bottom cell. The surface of the samples were coated with a Pt catalyst. The cell is voltage biased with an integrated photovoltaic device and splits H₂O directly upon illumination using light as the only energy input. This solar-powered H₂O splitter converts ~ 12.5% of sunlight energy to gaseous fuel.

Dinuclear Cyclometallated Platinum(II) Complex as a Sensitive Luminescent Probe for SDS Micelles

L.-Z. WU, T.-C. CHEUNG, C.-M. CHE, K.-K. CHEUNG and M. H. W. LAM, *Chem. Commun.*, 1998, (10), 1127–1128

The photoluminescent properties of two dinuclear cyclometallated Pt(II) complexes, [Pt₂L₂(μ-dppm)]²⁺ (1) and [Pt₂L₂(μ-dppm)]²⁺ (2), were studied in SDS micellar solution. The emission properties of (1) were dramatically altered by the addition of a counter cation. Initial addition of NaCl slightly enhanced the intensity and lifetime of the 530 nm emission, while with further NaCl, an additional emission maximum gradually developed at 650 nm. (1) was found to undergo enhancement of luminescence as well as switching of emissive states upon incorporation in SDS micelles.

New Binding State Useful for Attachment of Dye-Molecules onto TiO₂ Surface

M. LI, Z. XIAO, Z. HUAN and Z. LU, *Appl. Surf. Sci.*, 1998, **125**, (2), 217–220

Two novel Ru polypyridyl complexes, [(bpy)₂Ru(phen-dione)](PF₆)₂ and [(bpy)₂Ru(phen-dioxime)](PF₆)₂, which contain carbonyl and oxime groups, respectively, have been prepared and anchored onto TiO₂ surfaces. IR and absorption spectra showed favourable interfacial binding between the dye molecules and the TiO₂ surface and very high IPCE (incident monochromatic photo-to-current conversion efficiency) values were obtained.

ELECTRODEPOSITION AND SURFACE COATINGS

Platinum Deposition on Carbon Nanotubes via Chemical Modification

R. YU, L. CHEN, Q. LIU, J. LIN, K.-L. TAN, S. C. NG, H. S. O. CHAN, G.-Q. XU and T. S. A. HOR, *Chem. Mater.*, 1998, **10**, (3), 718–722

C nanotubes can be modified by the oxidation of HNO₃ or a H₂SO₄-HNO₃ mixture. The latter is more effective in producing a high density of surface functional groups which act as specific nucleation sites thus allowing the deposition of well-dispersed Pt clusters from PtCl₂, useful for catalysis.

Effect of O₂ Addition on the Deposition of Pt Thin Films by Metallorganic Chemical Vapor Deposition

J. M. LEE, C. S. HWANG, H.-J. CHO, C.-G. SUK and H. J. KIM, *J. Electrochem. Soc.*, 1998, **145**, (3), 1066–1069

Crystalline Pt thin films were deposited on SiO₂/Si at 325°C by low-pressure MOCVD using Pt-hexafluoroacetylacetonate as a precursor. The addition of O₂, above a critical flow rate of 50 sccm, was needed to give dense Pt thin films with smooth surfaces and high electrical conductivity. The wettability of the Pt thin films on SiO₂/Si was improved and the grain growth suppressed by post annealing with increasing addition of O₂ during deposition. O₂ enhanced the decomposition of the precursor and oxidised the Pt films.

Studies of Platinum Electroplating Baths. Part V: Solutions Derived from Pt(NO₂)₂²⁻ in Aqueous Acid

W. LEVASON, D. PLETCHER, A. M. SMITH and A. R. BERZINS, *J. Appl. Electrochem.*, 1998, **28**, (1), 18–26

An electroplating bath, with Pt(NO₂)(H₂O)₂⁺ as the major Pt(II) species (concentration 6 g dm⁻³), was formed by dissolving Pt(NO₂)₂²⁻ in methanesulfonic acid, despite difficulties in displacing the final nitrite ligand. Pt coatings could be formed at room temperature, and adhesive and reflective deposits formed at very moderate temperatures, ~ 318 K, compared to both P- and Q-baths which must be operated at > 363 K. At 343 K, good quality coatings can be obtained with current densities of 1–15 mA cm⁻².

Preparation of Palladium Composite Membranes by Modified Electroless Plating Procedure

H.-B. ZHAO, K. PFLANZ, J.-H. GU, A.-W. LI, N. STROH, H. BRUNNER and G.-X. XIONG, *J. Membrane Sci.*, 1998, **142**, (2), 147–157

A thin Pd composite membrane was produced by modified electroless plating involving the activation of a ceramic substrate by the sol-gel process of a Pd(II)-modified boehmite sol. The adherence of the Pd layer to the substrate was improved by the infiltration of an electroless plating solution to a porous substrate during Pd deposition. The resulting membrane had a thickness of ~ 1 μm and a high compactness, with a H₂ selectivity of 20–130 for H₂/N₂ and a H₂ flux of 1.8–87 m³ m⁻² h⁻¹, depending on operating conditions.

Electrochemical Deposition of Iridium(IV) Oxide from Alkaline Solutions of Iridium(III) Oxide

J. E. BAUR and T. W. SPAINE, *J. Electroanal. Chem.*, 1998, **443**, (2), 208–216

Hydrous Ir oxide films were deposited onto glassy C electrodes from a basic solution of saturated Ir(III) oxide by cyclic voltammetry. An acidic solution of Ir(OH)₂Cl₂⁻ was prepared from IrCl₆³⁻ or IrCl₆²⁻ and then made basic, to deposit Ir(IV) oxide via oxidation by O₂ generated from hydroxide. A strongly adherent, bright blue deposit of Ir oxide was formed after 10–20 scans at -0.3 to + 1.0 V vs. Ag/AgCl.

APPARATUS AND TECHNIQUE

Polycarbazole-Based Electrochemical Transistor

V. RANI and K. S. V. SANTHANAM, *J. Solid State Electrochem.*, 1998, 2, (2), 99–101

A polycarbazole conducting polymer transistor was fabricated using polymer-coated Pt plates as the source and drain. The transistor is small, has a redox potential of 1.30 V and an inter-electrode spacing of 200–500 μm . This device has a high saturation current region in the most positive bias voltage (1.3 V), with negligible hysteresis and greater stability.

Photomodulated Thermoreflectance Detection of Hydrogen Gas Using Optically Thin Palladium Film on Silicon Oxide

K. KALLI, A. OTHONOS, C. CHRISTOFIDES, A. SPETZ and I. LUNDSTRÖM, *Rev. Sci. Instrum.*, 1998, 69, (3), 1505–1511

The sensitivity of 8, 100 and 500 nm optically thin Pd layers evaporated on a Si oxide substrate was studied in the presence of H_2 /air at room temperature. The magnitude of the resulting reflectivity change was measured using an excite-probe technique, through laser excited photothermal modulation of a probe beam. With the 8 nm Pd film, concentrations of 0.1% H_2 may be measured in the presence of a balanced air mixture at room temperature.

Improved Passivating Cr_2O_3 Scales for Thin Film High Temperature PdCr Strain Gages

S. E. DYER, O. J. GREGORY and J. D. COOKE, *Thin Solid Films*, 1998, 312, (1/2), 331–340

The performance of high temperature, thin film PdCr strain gauges is greatly improved by enhancing the passivating nature of Cr_2O_3 formed on the sensor surface. PdCr gauges with sputtered Cr overcoats withstood 12,000 strain cycles of 1100 μe during 100 h of testing at 1000°C. Gauge factors of 1.3 with drift rates as low as 0.1 $\Omega \text{ h}^{-1}$ were achieved for devices with a nominal resistance of $\sim 100 \Omega$. Temperature coefficients of resistance (TCRs) of +550 ppm °C⁻¹ to +798 ppm °C⁻¹ were observed, depending on the physical and thermal properties of the films.

Electrical Characteristics of CO_2 -Sensitive Diode Based on WO_3 and IrO_2 for Microsensor Applications

S. CHAO, *Jpn. J. Appl. Phys., Part 2 Lett.*, 1998, 37, (2B), L245–L247

Devices based on the contact of sputtered WO_3 and IrO_2 that are covered by a HCO_3^- -containing polymer exhibit reversible and reproducible CO_2 -dependent, diode-like current rectification at 1 atm and room temperature. The gain or loss of current in the forward direction as a function of CO_2 concentration is found to be tunable by controlling the thickness ratio of the WO_3 and IrO_2 films. The rectification mechanism is uniquely ruled by the thermodynamic free energies. The diodes are useful for fabricating durable microsensors operating in gases or liquids.

Fiber-Optic Oxygen Sensor Based on the Fluorescence Quenching of Tris(5-acrylamido, 1,10 phenanthroline) Ruthenium Chloride

K. P. MCNAMARA, X. LI, A. D. STULL and Z. ROSENZWEIG, *Anal. Chim. Acta*, 1998, 361, (1–2), 73–83

A new acrylate Ru diimine complex, tris(5-acrylamido, 1,10 phenanthroline) Ru chloride (1), is described, where the acrylate functional group is used to co-polymerise the Ru dye with acrylamide, to produce an O_2 sensitive polymer. (1) maintains its full O_2 response with a slight decrease in its quantum yield for emission. A great improvement in the stability of fibre-optic O_2 sensors using (1) as an O_2 sensitive fluorescence indicator was observed. Samples with increased hydrophobicity were more stable.

HETEROGENEOUS CATALYSIS

Effect of Pt Dispersion on the Reduction of NO by Propene over Alumina-Supported Pt Catalysts under Lean-Burn Conditions

J.-H. LEE and H. H. KUNG, *Catal. Lett.*, 1998, 51, (1, 2), 1–4

The reduction of NO by propene under lean-burn conditions and the oxidation of NO were studied on two Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts with 4.4% and 82% Pt dispersion. At 265°C, the turnover frequency for the oxidation of NO to NO_2 was $> 50 \text{ min}^{-1}$ on the low dispersion catalyst and 0.3 min^{-1} on the high dispersion sample. This difference was less pronounced for the reduction of NO where the $\text{N}_2\text{O}/\text{N}_2$ ratio in the product was found to increase with hydrocarbon conversion.

Platinum-Added Sulfated-Zirconia Effective for Highly Selective Dehydrogenative Coupling of Methane

T. KUROSAKA, H. MATSUHASHI and K. ARATA, *Chem. Lett. Jpn.*, 1998, (3), 265–266

An active and stable 3 wt.%Pt- SO_4/ZrO_2 for the dehydrogenative coupling of CH_4 was prepared by impregnating ZrO_2 gel with H_2PtCl_6 solution, followed by calcination in air and reduction in H_2 . This catalyst gave 40% conversion of the equilibrium value with 100% selectivity at 500°C.

In Situ Synthesis and the Catalytic Properties of Platinum Colloids on Polystyrene Microspheres with Surface-Grafted Poly(*N*-isopropylacrylamide)

C.-W. CHEN, M.-Q. CHEN, T. SERIZAWA and M. AKASHI, *Chem. Commun.*, 1998, (7), 831–832

Well dispersed Pt colloids were synthesised in situ on polystyrene microspheres with surface-grafted poly(*N*-isopropylacrylamide) (PS-PNIPAAm) by the reduction of PtCl_6^{2-} with EtOH. This gave an average particle size and size distribution of 15.0 and 5.6 Å, respectively, which are smaller than Pt colloids protected by free PNIPAAm. These particles were used as catalysts for the hydrogenation of allyl alcohol in H_2O . The PS-PNIPAAm catalyst showed higher activity than commercial Pt/C and Pt colloids on PS beads and retained high activity after recycling 7 times.

Performance and Structure of Pt-Rh Three-Way Catalysts: Mechanism for Pt/Rh Synergism

Z. HU, F. M. ALLEN, C. Z. WAN, R. M. HECK, J. J. STEGER, R. E. LAKIS and C. E. LYMAN, *J. Catal.*, 1998, **174**, (1), 13–21

Fresh Pt and Rh catalysts were found to be highly active for three-way conversions of HC/CO/NO. After exposure to exhaust at elevated temperature, the Pt and Rh catalysts deteriorated, and only the aged Pt-Rh catalyst (1) remained highly active. For (1), the Pt and Rh are subjected to the same deactivation cycles as the individual Pt and Rh catalysts, but the Rh in aged (1) can regenerate in exhaust at ~ 560 K, which is much lower than the normal operating temperature. This is attributed to H₂/CO spillover on Pt particles in (1) which allows the regeneration of the inert Rh-aluminate species to active Rh metal particles.

Palladium-Catalyzed Coupling Reactions of 1-Bromoadamantane with Styrenes and Arenes

S. BRÅSE, B. WAEGELL and A. DE MEIJERE, *Synthesis*, 1998, (2), 148–152

The reaction of 1-bromoadamantane (1) with styrene and donor-substituted styrenes in the presence of a Pd/C catalyst gave the corresponding Heck-type coupling products in moderate yields (15–41%). However, the reaction of (1) with various arenes over Pd/C gave the corresponding adamantyl-substituted arenes in good to excellent yields (35–98%). This Pd-catalysed coupling of bridgehead adamantyl bromides with styrenes, etc., provides a convenient and clean way of preparing bridgehead derivatives of adamantane.

Effect of K₂O on a Pd-Containing Catalytic Converter for Removing CO and HC Emissions from a Two-Stroke Motorcycle

C.-H. LEE and Y.-W. CHEN, *Ind. Eng. Chem. Res.*, 1998, **37**, (4), 1260–1266

The effects of K₂O on Pt, Pd and Rh catalysts supported on Al₂O₃, K₂O/Al₂O₃, CeO₂/Al₂O₃ and K₂O/CeO₂/Al₂O₃ were studied for CO and hydrocarbon oxidation. Under the stoichiometric point, the Pd-containing catalysts had higher activity than those containing Pt for both CO and C₃H₆ oxidation, with Pd/K₂O/CeO₂/Al₂O₃ being the most active. CO conversion is promoted by K₂O. CO conversion over PdRh/K₂O/Al₂O₃-CeO₂ is very close to that of a typical two-stroke motorcycle catalytic converter.

Silica-Supported Phosphine Palladium(0) Complex Catalyzed Phenylation of Acid Chlorides and Aryl Iodides by Sodium Tetraphenylborate

M.-Z. CAI, C.-S. SONG and X. HUANG, *Synth. Commun.*, 1998, **28**, (4), 693–700

NaBPh₄ reacted with acid chlorides in the presence of a catalytic amount of a phosphine Pd(0)/SiO₂ under mild conditions to produce the corresponding phenyl ketones in 57–80% yield. The reaction with aryl iodides gave corresponding biaryls in 75–84% yield.

Methanol Synthesis from Syngas over Supported Palladium Catalysts Prepared Using Water-in-Oil Microemulsion

W.-Y. KIM, H. HAYASHI, M. KISHIDA, H. NAGATA and K. WAKABAYASHI, *Appl. Catal. A: Gen.*, 1998, **169**, (1), 157–164

The hydrogenation of CO was performed over Pd/ZrO₂ catalysts prepared using a H₂O-in-oil microemulsion. The catalyst prepared with a Pd concentration of 1.0 mol l⁻¹ had the smallest Pd particles (2.5 nm) and the highest activity for CO hydrogenation, giving ~ 3 times higher CO conversion than impregnated catalysts. Some of the Pd particles were wholly or partially embedded in the support. The activity of the catalyst increased as the amount of Pd exposed to the surface of the support increased.

Decomposition of Water-Containing Nitrous Oxide Gas Using Ru/Al₂O₃ Catalysts

X. F. WANG and H. C. ZENG, *Appl. Catal. B: Environ.*, 1998, **17**, (1–2), 89–99

Water-containing N₂O from nylon manufacture was decomposed in a tubular quartz reactor with 0.2 wt.% Ru/Al₂O₃ catalyst. Excellent catalytic activity was obtained for both dry and wet N₂O feeds and two activation processes were chosen: at low and high temperatures, with long and short activation times, respectively. The catalyst system was chemically and hydrothermally stable. Optimum catalyst performance can be achieved by cooling down the offgas of adipic acid manufacture to room temperature before being sent to the reactor, to remove extra H₂O content.

Wet-Oxidation of a Model Domestic Wastewater on a Ru/Mn/Ce Composite Catalyst

S. IMAMURA, Y. OKUMURA, T. NISHIO, K. UTANI and Y. MATSUMURA, *Ind. Eng. Chem. Res.*, 1998, **37**, (3), 1136–1139

The performance of Mn/Ce and Ru/Ce catalysts was examined during catalytic wet-oxidation of a model domestic wastewater. A combination of both catalysts resulted in an increase in the catalytic activity with the highest activity being displayed by Ru/Mn/Ce containing 3 wt.% Ru and atomic ratio Mn:Ce of 1:9. The activity of the Ru/Mn/Ce catalysts was independent of their redox properties.

HOMOGENEOUS CATALYSIS

A Novel Ketone Synthesis by a Palladium-Catalyzed Reaction of Thiol Esters and Organozinc Reagents

H. TOKUYAMA, S. YOKOSHIMA, T. YAMASHITA and T. FUKUYAMA, *Tetrahedron Lett.*, 1998, **39**, (20), 3189–3192

The treatment of ethanethiol esters with PdCl₂(PPh₃)₂ (5 mol%) and organozinc reagents at room temperature gives a range of ketones. The reaction is compatible with a variety of functional groups, including esters, ketones, aromatic halides and aldehydes, giving the products in good to excellent yields.

Direct Homocoupling of Aryl Halides Catalyzed by Palladium

V. PENALVA, J. HASSAN, L. LAVENOT, C. GOZZI and M. LEMAIRE, *Tetrahedron Lett.*, 1998, **39**, (17), 2559–2560
Pd(OAc)₂/nBu₄NBr (0.05/0.5 equivalents) catalyses the Ullmann-type homocoupling of iodo- or bromoaryls substituted with various groups such as cyano, nitro, aldehyde, methoxy or halogen (Cl, F) to give symmetrical functionalised biaryls or bipyridines. Isolated yields of 42–95% were obtained after reaction times of 7–50 hours. This method allows the direct preparation of functionalised biphenyls or bipyridines from the corresponding halide with catalytic amounts of a metal derivative.

A New, Efficient, and in Some Cases Highly Regioselective Water-Soluble Polymer Rhodium Catalyst for Olefin Hydroformylation

A. N. AJJOU and H. ALPER, *J. Am. Chem. Soc.*, 1998, **120**, (7), 1466–1468

The H₂O-soluble complex Rh/PPA(Na⁺)/DPPEA (1) prepared from poly(4-pentenoic acid) (PPA) and bis[2-(diphenylphosphino)ethyl]amine (DPPEA) was found to be a highly active catalyst for the hydroformylation of higher olefins, especially vinylarenes. Some selectivity was observed for linear aldehydes in the hydroformylation of aliphatic olefins, while high ratios of branched aldehydes resulted from vinyl ethers. (1) is the first polymeric H₂O-soluble metal complex which can catalyse the conversion of vinylarenes to 2-arylpropanals with a high chemo- and regioselectivity.

Heck Reactions without Salt Formation: Aromatic Carboxylic Anhydrides as Arylating Agents

M. S. STEPHAN, A. J. J. M. TEUNISSEN, G. K. M. VERZIJL and J. G. DE VRIES, *Angew. Chem. Int. Ed.*, 1998, **37**, (5), 662–664

A Heck reaction which does not produce halide salts and economically produces aryl olefins by using aromatic carboxylic anhydrides as arylating agents, is described. The reaction uses a halide-activated PdCl₂ which requires no phosphane ligands, to give good yields of the resulting arylated olefins.

Rhodium Complexes with Dioximes as Catalysts of Hydroformylation and Hydrogenation of 1-Hexene

M. MOSZNER, A. M. TRZECIAK and J. J. ZIÓLKOWSKI, *J. Mol. Catal. A: Chem.*, 1998, **130**, (3), 241–248

The Rh(II) dioxime complexes [Rh(Hdmg)₂(PPh₃)₂] (1) and [Rh(Hdmg)(ClZndmg)(PPh₃)₂] (2) (Hdmg = monoanion of dimethylglyoxime) catalyse the hydroformylation and hydrogenation of 1-hexene at 1 MPa CO/H₂ and 0.5 MPa H₂ at 353 K, respectively. Hydroformylation with (1) gave 94% aldehydes and 6% 2-hexene. RhH(Hdmg)₂(PPh₃) (3) had similar activity to (1). Complexes (1), (2), (3) and [Rh(Hdmg)₂(PPh₃)₂]ClO₄ catalyse 1-hexene hydrogenation with an average TON of ~ 18 cycles mol⁻¹ [Rh] min⁻¹, while (2) was also active for hydrogenations of cyclohexene, 1,3-cyclohexadiene and styrene.

A New Efficient Access to Glycono-1,4-lactones by Oxidation of Unprotected Itols by Catalytic Hydrogen Transfer with RhH(PPh₃)₄-Benzalacetone System

I. ISAAC, G. AIZEL, I. STASIK, A. WADOUACHI and D. BEAUPÈRE, *Synlett*, 1998, (5), 475–476

The treatment of unprotected pentiols and hexitols by catalytic H₂ transfer using RhH(PPh₃)₄ (1) as a catalyst and benzalacetone as a H acceptor, exclusively produced glycono-1,4-lactones under mild conditions in 60–96% yield. The treatment of *meso* erythritol with (1) and benzalacetone in DMF at 60°C led to a racemic mixture of D,L-erythrono-1,4-lactone in 95% isolated yield.

Hydrogenation of Phenylacetylene Homologs Catalyzed by [RhH₂(Ph₂N₃)(PPh₃)₂] in Dimethyl Sulfoxide

T. YONEDA and N. KAMEDA, *Nippon Kagaku Kaishi*, 1998, (1), 30–35

The homogeneous hydrogenation of phenylacetylene homologs catalysed by [RhH₂(Ph₂N₃)(PPh₃)₂] (1) in dimethyl sulfoxide was studied at 1 atm H₂ and 303 K. (1) actively catalysed the hydrogenation of terminal and internal alkynes to alkenes, with terminal alkynes more easily reduced than internal ones. The initial hydrogenation products of internal alkynes were *cis*- and *trans*-alkenes, with *cis* being more abundant. After the yield of *cis*-alkenes reached a maximum, the yield of *trans*-alkenes increased rapidly accompanied by the decrease of the *cis*-alkenes.

Asymmetric Synthesis of 2,3-Dihydrofurans by Reaction of Rhodium-Stabilized Vinylcarbenoids with Vinyl Ethers

H. M. L. DAVIES, G. AHMED, R. L. CALVO, M. R. CHURCHILL and D. G. CHURCHILL, *J. Org. Chem.*, 1998, **63**, (8), 2641–2645

The decomposition of 2-diazo-3-siloxybutenoates, containing (*R*)-pantolactone as a chiral auxiliary, in the presence of vinyl ethers, and Rh(II) octanoate, Rh₂(OOct)₄, as catalyst, results in the highly diastereoselective synthesis of cyclopropanes. Desilylation of the cyclopropanes with nBu₄NF results in ring expansion of the resulting acylcyclopropanes to give 2,3-dihydrofurans with retention of stereochemistry.

An Unusual Enhancement of Catalytic Activity in Biphasic Catalysis: The Rhodium Catalyzed Hydroformylation of Acrylic Esters

G. FREMY, E. MONFLIER, J.-F. CARPENTIER, Y. CASTANET and A. MORTREUX, *J. Mol. Catal. A: Chem.*, 1998, **129**, (1), 35–40

A H₂O soluble Rh complex of a trisulfonated triphenylphosphine was used for the hydroformylation of various acrylic esters in a two-phase system. The hydroformylation rates of acrylates that were relatively soluble in H₂O were surprisingly higher in the biphasic system than those observed under comparable homogeneous conditions; rate enhancement by a factor of 2–14 was observed. The role of H₂O on the enhancement of catalytic activity is discussed.

The Regiochemistry of Reduction of Mono-Ethyl Fumarate and Maleate Using a Ruthenium BINAP Catalyst

M. SHAHARUZZAMAN, J. BRADDOCK-WILKING, J. S. CHICKOS, C. N. TAM, R. A. G. D. SILVA and T. A. KEIDERLING, *Tetrahedron: Asymmetry*, 1998, 9, (7), 1111-1114

The regiochemistry of the reduction of mono-ethyl fumarate using *bis*(carboxylato){2,2'-*bis*(diphenylphosphino)-[R]-1,1'-binaphthyl}-Ru(II) (Ru[BINAP]) in H₂/CH₃OD was found to occur with opposite regiochemistry to that observed in the reduction of tiglic acid. Reduction of mono-ethyl maleate with D₂/CH₃OD was very sluggish but produced *meso*-dideuteriosuccinic acid with high stereoselectivity. Reduction of mono-ethyl maleate with Ru[BINAP](O₂CR)₂ and H₂/CH₃OD resulted in mono-ethyl succinate-d, with nearly complete loss of regioselectivity.

Ruthenium-Catalyzed Isomerization of Homoallylic Alcohols in Water

D. WANG, D. CHEN, J. X. HABERMAN and C.-J. LI, *Tetrahedron*, 1998, 54, (20), 5129-5142

The regioselective rearrangement of homoallylic alcohols to allylic alcohols and the isomerisation of allylic alcohols are efficiently catalysed by RuCl₂(PPh₃)₃ in H₂O under air. The product selectivity is affected by temperature and amount of catalyst with higher temperatures and small amounts of catalyst (2 mol%) being preferable. A tandem olefin migration-allylic rearrangement mechanism is postulated.

FUEL CELLS

Porosity and Catalyst Utilization of Thin Layer Cathodes in Air Operated PEM-Fuel Cells

A. FISCHER, J. JINDRA and H. WENDT, *J. Appl. Electrochem.*, 1998, 28, (3), 277-282

The introduction of additional porosity into thin film electrodes for PEMFCs improves the cell and cathode performance, in particular when air is the oxidant. The membrane-electrode assembly is prepared by a hot spraying method. This gives the O₂ better access from air to the inner surface of the electrode and leads to higher electrocatalyst utilisation. For air operation at ambient pressure and with a catalyst loading of 0.15 mg Pt cm⁻² a current density of 200 mA cm⁻² at a cell voltage of 0.7 V can be obtained.

Surface Structure Effects in Platinum/Ruthenium Methanol Oxidation Electrocatalysis

W. CHRZANOWSKI and A. WIECKOWSKI, *Langmuir*, 1998, 14, (8), 1967-1970

The catalytic activity of low-index Pt single-crystal faces, Pt(111), Pt(100), Pt(110) and polycrystalline Pt toward MeOH electro-oxidation was increased by controlled amounts of electrodeposited Ru. The most active surface was Pt(111) covered by 0.2 monolayers of Ru, with the TON at 80°C being ~ one order of magnitude higher than that from commercial Pt/Ru catalysts. The Pt(111)/Ru electrode was the best small scale fuel cell anode for MeOH oxidation.

Polymer Electrolyte Membranes Incorporated with Nanometer-Size Particles of Pt and/or Metal-Oxides: Experimental Analysis of the Self-Humidification and Suppression of Gas-Crossover in Fuel Cells

M. WATANABE, H. UCHIDA and M. EMORI, *J. Phys. Chem. B*, 1998, 102, (17), 3129-3137

Self-humidification behaviours of new polymer electrolyte membranes (PEMs): Pt-PEM, TiO₂-PEM, Pt-TiO₂-PEM, were studied in PEFCs operated with dry H₂ and O₂. The PEMs were prepared by dispersing small amounts of Pt and/or metal oxides, such as TiO₂, in Nafion. Performance of the cells with Pt-PEM or Pt-TiO₂-PEM could be improved at 1 A cm⁻² by 0.1 V at the anode and 0.2 V at the cathode resulting from homogenising the distribution. No, or minimal, humidification is necessary for PEFCs used as the power sources for electric vehicles or electronic devices.

CHEMICAL TECHNOLOGY

Reactivity of Permeating Hydrogen with Thiophene on a Palladium Membrane

M. SHIRAI, Y. PU, M. ARAI and Y. NISHIYAMA, *Appl. Surf. Sci.*, 1998, 126, (1/2), 99-106

The reactivity of H atoms, supplied by permeating through a Pd membrane, was investigated for the hydrodesulfurisation of thiophene and compared with H atoms supplied by dissociatively adsorbing on the Pd membrane from the gas phase. The first system showed higher activity. Permeating H atoms were higher in energy than co-adsorbed H atoms and the activation energy of the system was lower.

ELECTRICAL AND ELECTRONIC ENGINEERING

Low-Resistance Vertical Conduction Across Epitaxially Lifted-Off n-GaAs Film and Pd/Ge/Pd Coated Si Substrate

J. C. FAN, C. M. TSAI, K. Y. CHEN, S. Y. WANG, G. LIN and C. P. LEE, *J. Electron. Mater.*, 1998, 27, (3), 110-113

Insertion of a Pd/Ge/Pd interlayer between an epitaxially lifted-off (ELO) n-GaAs thin film and a Si substrate resulted in low-resistance ohmic conduction. Good bonding and ohmic contact were achieved after annealing. Pd/Si gave smooth and shallow ohmic contact to Si. Good laser performance was obtained, and ELO provides more flexible hybrid integration.

Pd/GaN Schottky Diode with a Barrier Height of 1.5 eV and a Reasonably Effective Richardson Coefficient

H. ISHIKAWA, K. NAKAMURA, T. EGAWA, T. JIMBO and M. UMENO, *Jpn. J. Appl. Phys., Part 2 Lett.*, 1998, 37, (1A/B), L7-L9

A Pd/GaN Schottky diode with excellent electronic properties was formed on high-quality GaN thin films by photolithography. The barrier height was 1.53 eV. The Richardson coefficient of 23.2 A cm⁻² K⁻² is almost equal to the theoretical value of 26 A cm⁻² K⁻².